Technical Support Package

Fiber-Optic Determination of N$_2$, O$_2$, and Fuel Vapor in the Ullage of Liquid-Fuel Tanks

NASA Tech Briefs
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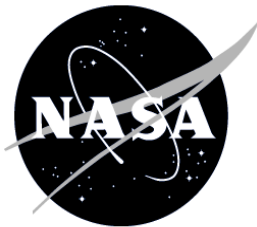
National Aeronautics and
Space Administration

Technical Support Package

for

FIBER-OPTIC DETERMINATION OF N_2, O_2, AND FUEL VAPOR IN THE ULLAGE OF LIQUID-FUEL TANKS

LEW-17826-1

NASA Tech Briefs

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Fiber-Optic Determination of N_2, O_2, and Fuel Vapor in the Ullage of Liquid-Fuel Tanks

Brief Abstract

A fiber optic sensor system that remotely measures the concentration of molecular oxygen, nitrogen, hydrocarbon vapor, and other gases in the ullage of a liquid fuel tank is described. The system provides an accurate and quantitative identification of the above gases with an accuracy of better than 1% (by volume) over approximately a 1 minute time duration. The technology described in this disclosure is a critically enabling sensor technology for the feedback control of on-board inert gas generation systems (OBIGGS) that are used to inert aircraft fuel tanks for the prevention of aircraft fuel tank explosions and fires such as the one responsible for the TWA Flight 800 tragedy. The system is simple, compact, lightweight, and can be made robust and reliable for aircraft use. Furthermore, this sensor technology does not present an intrinsic fire or explosion safety hazard compared to electrically-based sensors that require wiring.

Section I — Description of the Problem

See attached report "Fiber optically coupled spontaneous Raman scattering system for the determination of nitrogen and oxygen concentrations in the ullage of liquid fuel tanks" by Quang-Viet Nguyen, 10/15/2004.

Section II — Technical Description

See attached report "Fiber optically coupled spontaneous Raman scattering system for the determination of nitrogen and oxygen concentrations in the ullage of liquid fuel tanks" by Quang-Viet Nguyen, 10/15/2004.

Section III — Unique or Novel Features

See attached report "Fiber optically coupled spontaneous Raman scattering system for the determination of nitrogen and oxygen concentrations in the ullage of liquid fuel tanks" by Quang-Viet Nguyen, 10/15/2004.

Section IV — Potential Commercial Applications

Aircraft manufacturers will be interested in this system for use in the aircraft, especially if an OBIGGS is mandated by the Government. Smaller companies who make fuel systems and sensor components for the aircraft companies will also be interested. Sensor systems designed to ensure the safe operation of an aircraft tend to be expensive, as aircraft are expensive (at the time of this reporting in 2004, $20 M to $100 M price tag each is typical). The entire fleet of domestic commercial passenger aircraft in the U.S. is about 100,000 planes. A sensor system price tag ranging from $5,000 to $20,000 is a fair estimate of the system sales price and is not unreasonable. To add this system to each plane in the domestic fleet provides a potential market of $500 M to $2 B in sales.

At the time of this report, there was no technology that has been named by the F.A.A. to be the standard that is suitable for use on-board commercial aircraft. Consequently, many companies are developing technologies that they think will best provide an OBIGGS oxygen sensor. The technology described in this disclosure is the only one that can provide oxygen AND nitrogen, and even fuel vapor concentrations with good accuracy.

Fiber optically coupled spontaneous Raman scattering system for the determination of nitrogen and oxygen concentrations in the ullage of liquid fuel tanks

Attachment for Disclosure of New Invention and Technology Report

by

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Date: 10/15/2004

Attachment for Disclosure of New Invention and Technology Report

Fiber optically coupled spontaneous Raman scattering system for the determination of nitrogen and oxygen concentrations in the ullage of liquid fuel tanks

by
Quang-Viet Nguyen

Brief Abstract:

A fiber optic sensor system that remotely measures the concentration of molecular oxygen, nitrogen, hydrocarbon vapor, and other gases in the ullage of a liquid fuel tank is described. The system provides an accurate and quantitative identification of the above gases with an accuracy of better than 1% (by volume) over approximately a 1 minute time duration. The technology described in this disclosure is a critically enabling sensor technology for the feedback control of on-board inert gas generation systems (OBIGGS) that are used to inert aircraft fuel tanks for the prevention of aircraft fuel tank explosions and fires such as the one responsible for the TWA Flight 800 tragedy. The system is simple, compact, lightweight, and can be made robust and reliable for aircraft use. Furthermore, this sensor technology does not present an intrinsic fire or explosion safety hazard compared to electrically-based sensors that require wiring.

I. Description of Problem:

A. In the area of aircraft safety, there exists a need to reduce or eliminate the explosion hazard posed by the mixture of fuel vapors and oxygen contained in the space above the liquid (ullage) of a fuel tank. In a conventional aircraft fuel tank, the ullage will contain a mixture of jet fuel vapor and air. As the fuel is used up, more air from the outside is drawn in to fill the ullage created by the spent liquid fuel. In order for a fire or explosion hazard to exist, there needs to be three things: fuel, oxygen, and energy to ignite the mixture. Since we cannot remove the fuel, and we cannot ensure with absolute certainty that there are no ignition sources (such as static electricity, lightning, or even a terrorist strike); we are left with reducing or removing the oxygen. The oxygen is removed by displacing it with nitrogen enriched air that is produced from an on-board inert gas generation system (OBIGGS) that feeds nitrogen-enriched air into the fuel tank to eventually displace the oxygen. Such systems are expensive to operate continuously (from a fuel economy standpoint), and it also desirable to know when the fuel tank has been inerted to a safe level (typically less than 9% by volume). Thus a way to measure the relative or absolute oxygen and/or nitrogen concentrations in the ullage of fuel tank is needed.

B. The unique features if this problem are: the sensor system cannot introduce any intrinsic fire or explosion hazard such as would be the case with electronic wire-based sensors; the sensor system needs to provide a measurement of the oxygen concentration over a wide temperature (-40 C to 71 C) and pressure range (0.2 atm to 1.0 atm) corresponding to the conditions inside an airplane fuel tank over the flight envelope; the sensor needs to be reliable and robust; the sensor needs to be compact and lightweight in order to be fitted to an airplane's fuel system; the sensor should preferably also measure nitrogen and fuel vapor concentrations for a secondary check of the OBIGGS system performance; the system needs to work reliably and unattended with no

maintenance for up to 1 year (time between fuel tank service checks); the system should preferably be low-cost for deployment on the entire fleet of commercial aircraft. Specifically, the sensor needs to be able to measure the absolute concentration of O_2 at the following condition which represents the lowest absolute concentration of molecular oxygen in the flight envelope. The sensor needs to have a 1% measurement precision and accuracy in measuring 5% O_2 (by volume) at a temperature of -1 C and a pressure of 0.2 atm, with the balance gases being nitrogen and fuel vapor [Chang, 2004].

C. Prior art relied on electrochemical oxygen sensors or paramagnetism oxygen sensors. A newer technique uses the effect of oxygen fluorescence quenching on a dye that is fiber optically illuminated by a blue LED has been proposed (see for example Remillard et al. [1999] and references therein). Other new techniques have been proposed to use diode laser absorption spectroscopy near 760 nm to measure oxygen (see for example Sanders et al. [2001]).

D. The first two techniques above require exposing the ullage gases to a sensor that is connected to a wire which can potentially be a source of sparks or electrostatic ignition. Furthermore, the electrochemical sensor typically uses a heated element that reacts and consumes the oxygen that it is sensing, producing a fire hazard. The fiber optic fluorescence quenching sensors that utilize the intensity of an oxygen sensitive dye that is illuminated with a blue LED have also been proposed but this sensor is prone to large drifts when exposed to temperature changes. The drift of the fluorescence quenching type sensor is so great that it renders the technique ineffective for the reliable measurement of oxygen concentration in the ullage of a fuel tank. The diode laser absorption technique is problematic because it requires a diode laser to tune and lock onto specific oxygen absorption lines, the technique requires windows for optical access which can get dirty from fuel deposits. None of these techniques can measure both nitrogen and oxygen concentration to provide an accurate mixing ratio without having to assume that the balance is nitrogen. Also, none of these other techniques are able to provide fuel vapor concentration.

II. Technically Complete Description

A. Purpose and Description of Innovation:
The purpose of the innovation is to provide a quantitative and accurate measurement of the concentration of nitrogen, oxygen, and fuel vapor in the ullage of a fuel tank. This information is needed in order to provide control information for an OBIGGS, and also for the determination of the appropriate levels of inerting required for safety. The ullage gas sensor system is based on spontaneous vibrational laser Raman scattering from the species of interest. Raman scattering is used because it is one of the few optical techniques that permits the simultaneous multi-species measurements of chemical concentrations.

B. Identification of Components and Parts:
The Raman scattering is implemented using fiber optic coupling which does not pose an intrinsic explosion or fire hazard. In addition, fiber optic coupled Raman scattering permits the sensor probe to be located remotely from the laser and spectrograph. Figure 1 shows a schematic of the overall system which uses a compact continuous wave (CW) diode pumped solid state (DPSS), or similar laser with 532 nm emission. Although a pulsed laser (Q-switched) can be used to provide similar laser powers on average, pulsed lasers should not be used since they have high

peak powers which pose an ignition problem. The laser is lens-coupled into a multi-mode 200 μm dia core fiber, which is the central fiber of a 7 fiber bundle arranged in a hexagonal-closest-packed geometry (shown in Fig. 2), that exposed to the ullage of a fuel tank. The Raman scattered light is collected by 6 fibers located around the central fiber (see Fig. 2) via proximity focusing. All fibers used are 0.22 numerical aperture (NA), Cu-clad, 200 μm core dia silica, optimized for visible wavelength transmission. The collection fibers are directed to a Raman spectrograph as shown in Fig. 1 which filters the Rayleigh (elastic) scattered light using a notch filter and disperses the Raman (in-elastic) scattered light into different wavelengths which are detected using a multi-channel light detector such as a CCD array. The signal from the detector is processed with an electronic circuit and/or a computer and software to provide a quantitative measure of the species concentration of N_2, O_2, and fuel vapor. The vibrational Raman bands for N_2, O_2, and hydrocarbon fuel vapor (such as jet fuel) are centered at the following wavelengths: 607 nm, 580 nm, 630 nm, respectively for 532 nm wavelength excitation. In order to collect the full vibrational band for each species, the spectral integration width for each vibrational band should be about 13 nm wide full-width-half-max (FWHM). These 13 nm wide spectral bands centered at the wavelength for each species can be referred to as a 'superpixel'. In the case of a detector plane that is fitted with discrete fiber optic collection devices leading to discrete light detectors, or a detector plane fitted with discrete light detectors such as photomultiplier tubes (PMT) or avalanche photodiodes (APD), the same spectral width and center locations still have to be used in order to maximize the signal while minimizing the effects of spectral cross-talk or interference.

The light directed into the spectrograph from the fiber bundle is arranged in a linear array as shown in Fig. 3 to maximize the optical throughput to the spectrograph by proper alignment with the spectrograph slit-axis. Figure 4 shows a detail of the fiber optic probe sensor tip which includes a means of preventing liquid fuel from entering and interfering with the gas-phase Raman measurement. Shown is a porous (gas permeable) cover that is made of a sintered polymer material or a PTFE membrane such as Gore-Tex brand industrial filters mounted onto a suitable membrane holder/support structure. The purpose of the gas permeable cover is to prevent liquid fuel droplets from directly contacting the faces of the fiber optic lines. This would cause the Raman scattered signal to come from the liquid only and would not represent the gas-phase molecules.

The Raman signal provided from the CCD array (or other type of detector) is then processed using electronic circuitry or with a computer and software. The basic processing algorithm for an array detector is shown in Fig. 5 and is as follows: (1) start the time integration process and collect the Raman spectrum over time period given by t_{int} (60 to 90 sec); (2) calculate the spectrally integrated signals using the superpixel definition (8); (3) calculate the quantitative number density for each species from the calibration Raman data (6) acquired previously; (4) using the ideal gas law, correct for the ambient pressure and temperature effects using the peripheral instrumentation data from the fuel tank (7); (5) provide a value for the concentration of N_2, O_2, and fuel vapor to the OBIGGS control system at an interval determined by the integration time set in step (1) which is typically 60 to 90 seconds. Note that a sliding-window integration time may be used in the case of discrete detectors that have a continuous data output (such as PMT's or APD's) representing photon counts. For this type of detection scheme, a continuous sliding-window allows a faster update time than t_{int}, by indicating the trend of the change in the signals. However, the full amount of time given by t_{int} must be used to make a determination of the concentration within the required precision.

C. Functional Operation:

In operation, the sensor probe is mounted into a fuel tank using a bulkhead feed through fitting or a flange type mount depending on the physical dimensions of the probe sensor body. The laser and spectrograph/detector can be remotely mounted away from the harsh environment of the fuel tank (such as in the avionics/instrumentation cabinet). The Raman signal collected by the sensor probe is continuously analyzed and accumulated in software or by using a sliding integration window that ranges from about 60 to 90 seconds wide. The value of the concentrations determined by the processor unit utilizing the algorithm described in Fig. 5 is then used to control the rate of inerting gas produced by the OBIGGS, and can also be used to determine the level of safety that exists in the fuel tank being monitored by the sensor system.

D. Alternate Embodiments:

Figure 6 shows an alternate embodiment that uses discrete detectors instead of an array detector as shown in Fig. 1. The discrete detectors have the potential advantage of lower costs, and of providing a continuous signal stream compared to the CCD array which has to be integrated on-chip, during which time, no signal is produced. The continuous stream signal from discrete detectors can be used in a sliding-window time integration scheme (in hardware or software) to provide a real-time indication of the concentrations in the fuel tank. Figure 7 shows a spectrograph with a prism-grating (GRISM) type spectrograph which has the advantage of being more compact and easier to align as it provides an undeviated central ray. The GRISM spectrograph also is capable of providing extremely high optical throughput (as fast as f/1.0) if high-speed photographic camera lenses are used. It is not the intent of this invention disclosure to make any claims as to spectrograph designs, but to claim that different types of high speed spectrographs may be used. Figure 8 shows an alternate embodiment of a polychromator that uses a series of dichroic mirrors or beam splitters to successively split the different wavelengths of Raman scattered light to discrete detectors (or fiber optic inputs) fitted with spectral band pass filters (each centered at 580 nm, 607 nm, and 630 nm with a 13 nm (FWHM) bandwidth). The dichroic mirrors can be thin-film coated type mirrors that transmit a longer wavelength while reflecting a shorter wavelength. Such mirrors are often used for color separation processes. In Fig. 8, the first dichroic mirror DM1 reflects wavelengths shorter than 590 nm and transmits wavelengths that are longer; the second dichroic mirror DM2 reflects wavelengths shorter than 615 nm and transmits wavelengths that are longer. In this way, the Raman signal from O_2 is directed to the first detector, N_2 to the second detector, and fuel vapor to the third detector. The advantages of this type of polychromator include the simplicity of the optical components, its insensitivity to optical misalignment, and a high optical throughput that can approach that of prism or grating based dispersion designs.

Figure 9 shows an alternate embodiment of the sensor probe tip that can be used to prevent the infiltration of liquid onto the fiber end faces. In Fig. 9, the tip of the sensor probe is mounted inside a cylindrical body that is much larger in diameter than the probe body. This cylindrical housing is fitted with a series of baffles and labyrinth plates that serve to prevent the direct line-of-sight impingement of liquids to the gas permeable membrane mounted behind the successive baffles and labyrinth plates. The labyrinth plates are essentially perforated plates specially designed so that their spacing is conducive to liquid wetting while at the same time, providing ridges and other specially designed surface protrusion that promote the liquid to drip off the labyrinth plates by gravity so that it can exit the drain holes located at the bottom of each

baffle plate chamber. Although not shown, each drain hole itself is baffled to prevent direct liquid entry through the bottom. The final gas permeable membrane(s) are bonded to a perforated plate that provides the structural integrity for the membrane. The membrane can be made of a polymer or material with a structure that permits gases to pass through but not liquids (such membranes are commercially available such as Gore-Tex brand industrial filters). In this design, provision can be made to include a small angled jet directed at the fiber faces, but not blocking the light path, to allow the period cleaning of the fiber faces by injection of a solvent (such as acetone, etc.). Furthermore, a small vent is provided to drain the contaminated solvent and to allow an exit path for the gas purge cleaning process. Finally, the cleaning and vent tubes permit the in-situ periodic calibration of the system by allowing the admission of a zero and span gases. Note that the cleaning and vent tubes are only opened during the cleaning or calibration process, and are normally closed. The valving operation for the cleaning and calibration procedures can be automated using computer controlled solenoid valves located externally to the fuel tank. Another benefit of this embodiment shown in Fig. 9 is that a large volume beyond the fiber face is provided which does not contribute to a Raman or Rayleigh scattering signature as would be the case from the membrane or porous cover placed in direct vicinity of the probe tip. Since the collection efficiency of the fiber falls off as $1/r^2$, by permitting a sufficient distance of about 10 to 20 cm beyond the fiber face prevents Raman scattering from the gas permeable cover surface to interfere with the gas phase Raman signal.

E. Supporting Theory:

The theory for Spontaneous Raman scattering is well known, see for example, Eckbreth [1988] and references therein. For the purposes of estimating Raman scattering signals for gas density measurements, the vibrational Raman scattering signal S (photon-counts) from a molecular species i over a certain period of time can be simplified to the following engineering relationship:

$$S_i = E_{LASER} C_{SYS} \Omega_{COLL} V_{PROBE} K_i N_i \ , \tag{1}$$

where E_{LASER} is the laser energy in Joules (J), C_{SYS} is an overall system collection constant that represents the optical to photo-electron (photon-count) efficiency per unit scattering cross-section·Joule (photon-counts $cm^{-2} J^{-1}$), Ω_{COLL} is the collection solid angle in steradians (sr), V_{PROBE} is the volume of the probed molecules (cm^3), K is the Raman scattering cross-section per unit molecule·steradian (cm^2 molec^{-1}sr^{-1}), and N is the number density (molec cm^{-3}). Equation (1) states that the Raman scattering signal is proportional to the laser energy, the molecular species, the volume of the probed molecules, and the number density of the molecular species. This relationship says that if we want to maximize the very weak signals from Raman scattering, we must maximize the laser energy, the collection efficiency, collection solid angle, and the probed volume, with everything else being equal. State of the art gas-phase Raman scattering systems such as those described by Miles [1999] provide about 18,300 photon-counts per Joule of 532 nm light for ambient N_2 using an approximate 10 ns long laser pulses (ca. 100 MW power). If we use a low power (20 – 30 mW) CW laser, over a period of 90 seconds, delivers 1.8 J of energy. However, a 20 – 30 mW power level is low enough so that it does not serve as an ignition source, provided that it is not focused to a small spot (the analysis of the ignition potential will be discussed in detail in a later section). Furthermore, over a period of 90 seconds, the thermal dissipation of the laser light over a large area prevents any significant thermal

buildup that can lead to ignition. The collection efficiency and solid angle are further increased by use of multiple fibers arranged around a central illumination fiber, which also serves to increase the collection volume for the signal. Finally, by using highly sensitive backside-illuminated CCD array detector, we can increase the quantum efficiency of the detector. Using the estimate given by Miles [1999] and the present CW fiber coupled system, we can expect approximately 32,000 photon-counts with the 20 mW CW laser system over a 90 second integration span. Since Raman scattering is described by Poisson statistics, the root-mean-square (rms) standard deviation of this signal is simply the square root of 32,000, which is 179, or a 0.56% precision.

F. The engineering specifications for the present system are:

1. A laser source for providing the Raman excitation is required. In the present embodiment a CW 20 mW 532 nm diode pumped solid state (DPSS) Nd:YVO$_4$ laser (Power Technologies Inc., model LCM-S-111-20). A second identical laser source but with 30 mW power was also used and will probably be the preferred laser due to the higher power output.

2. A means of transmitting the said laser light into the ullage via fiber optic probe is required. The same fiber optic probe is also used to collect the scattered light resulting from the Raman effect of the excitation laser light with the molecules being probed. This is accomplished with a custom made fiber optic bundle probe with qnty 7 x 200 micron core copper-clad silica optical fibers (0.22 NA), with the central fiber used for excitation and the surrounding 6 fibers used for collection, fibers surrounded by a flexible stainless coil sheath (Romack Inc.).

3. In order to disperse or separate the individual contributions of each vibrational Raman band for each species, a spectrograph or similar device is required. In the present embodiment a high optical throughput Raman spectrograph (f/1.8) with holographic grating (Kaiser Optical Systems Inc., Holospec f/1.8i) fitted with a holographic Rayleigh rejection filter (Kaiser Optical Systems Inc., SuperNotch+) with an optical density of 10^6 at 532 nm is used. Note that a compact, ruggedized spectrograph with integrated CCD detector such as those commercially available from companies such as Ocean Optics or B&W Tek, may also be used.

4. In order to detect the weak Raman scattering signals that are separated by the spectrograph, a high sensitivity liquid nitrogen cooled 1340x100 pixel backside-illuminated CCD detector with approximate 90% QE (Roper Scientific, Princeton Instruments Spec-10) is used in the present embodiment. However, a thermo electrically cooled CCD detector would be sufficient for the circa 1 minute long integration times. In the case of an integrated spectrograph/detector as described above (from Ocean Optics Inc. or B&W Tek Inc.), a separate detector is not needed.

5. In order to prevent the contamination of the fiber optic probe tip face with liquid fuel or other liquids, a gas permeable probe tip cover is required. The probe tip cover can be made of a sintered polymer material or a polymer membrane such as PTFE Gore-Tex type filter membranes such that will admit the free passage of gases such as N$_2$, O$_2$, and fuel vapor but not permit the passage of liquids. Other type of porous materials may include aerogel type porous materials, or plasticized aerogels.

However, the above specifications do not restrict this technology in the following ways:

1. The laser source can be any wavelength from 266 nm to 1064 nm, and can be a diode laser such as those with emission at or near 405 nm, 635 nm, 670 nm, 780 nm, 820 nm, etc, or a gas laser such as a HeNe, HeCd, Ar-ion, or other solid-state laser material including Nd:YAG, Nd:YLF, etc.

2. The fiber optic assembly is not limited to 7 fibers but can be any number ranging from 2 to 30, and not limited to 200 μm core diameter but can range from 5 μm to 1000 μm; and does not have to be made of silica but can be sapphire, or fluoride glass, etc. Furthermore, the illumination can be provided by more than one fiber ranging from 2 to 10 and furthermore, the illumination fiber can be single-mode in addition to multi-mode. In addition, the NA of the fiber is not limited to 0.22 but can be lower or higher depending on the fiber material used. However, it is important to match the NA to the f/# of the optics used in the high speed spectrograph. The relationship of $f/\# = (2\ NA)^{-1}$, states that in the case of 0.22 NA, the equivalent f/# is f/2.27. Thus the optics used in the spectrograph should be at least as fast. In the present embodiment f/1.8 optics are well matched to 0.22 NA fibers. In addition, the optical fibers are not limited to solid glass or solid crystal fibers but also include any similar light conduit such as a light pipe or hollow core fiber, or liquid filled light pipes.

3. The Raman spectrograph mode of operation can be of any type including: reflecting, transmission, etc. The dispersive element can be any type including: gratings (reflection and transmission), prisms, volume phase holographic, grating-prisms (GRISMS), or any combination thereof. The Rayleigh rejection filter can be any type including: colored glass filter, thin-film interference band pass, thin-film rugate type, volume phase holographic interference, molecular absorption filters, etc. or any combination thereof. The high speed spectrograph may also utilize a plurality of dichroic mirrors (or filters) that pass a longer wavelength while reflecting a shorter wavelength, used in combination with a transmission band-pass optical filter to separate the Raman vibrational bands centered at the wavelengths corresponding to oxygen, nitrogen, and fuel vapor at 580 nm, 608 nm, and 630 nm, respectively. Such systems do not require the use of an dispersive optical element such as a grating or prism.

4. The detector can be an array or discrete and can be any type of sensitive photoelectric device by which a photon is converted into an electrical signal. Such devices include photomultiplier tubes (PMT), avalanche photodiodes (APD), photodiodes, photovoltaic cells, CMOS detector arrays, microchannel detectors, image intensifier detectors, etc. In the case of discrete fibers or detectors though, the input aperture of the fiber or detector is adjusted such that its width satisfies the spectral bandwidth requirement of an approximately 13 nm spectral band pass for each Raman vibrational band that is collected.

5. The gas permeable cover can be a single piece unit or a multi-piece assembly and may contain multiple gas permeable membranes or porous solid materials or structures, with the common goal of preventing liquid entry into the area immediately surrounding the fiber faces of the probe tip. Additionally, baffles, tortuous passages, labyrinth seals, porous solid structures such as reticulated open-cell metal foams, plastic foams, ceramic foams, etc., can be used in combination with gas permeable membranes to further enhance the liquid separation function.

6. The measurement probe volume, although assumed to be the ullage of the fuel tank may also include any flow passages, piping or channeling that is connected to the ullage of the fuel tank. This includes the vent line or fill line connected to the ullage or a small chamber or vestibule connected to the ullage. In the case of OBIGSS nitrogen enriched flows from a separation unit, the fiber optic sensor probe head may be located within the pipe or tubing that is used to fill the ullage so that a determination of the O_2 concentration in the OBIGGS fill stream may be made.

G. Peripheral Items:

Peripheral items for this system include the temperature and pressure sensors that are required to calculate the absolute concentration of the gases as described in the previous section. Additionally, a means of monitoring and measuring the laser output power delivered into the optical fiber so that the normalization of the Raman signal may be performed is also required. Other peripheral items include the laser power supply, the signal processor or computer and software system for converting the raw Raman scattering signals into quantitative numbers representing the species concentrations. Other peripheral items may include an optional gaseous purge/cleaning system to enable in-situ cleaning of the fiber optic face on the probe tip.

H. Maintenance, reliability, safety factors:

The laser and optical systems in general are robust if hard mounted for flight use. The laser system is solid state and is very robust. It has a continuous operational lifetime of about 10,000 hours. Since it is fiber optically coupled, it may be services or replaced in a convenient location without having to access the fuel tank area in an aircraft. Such areas are usually very difficult to access. Furthermore, if multiple excitation fibers are used, then they can be connected to multiple and separate lasers for redundancy. Thus if one laser fails, another can be switched on in-flight without any down time. One area of concern is the cleanliness of the fiber optic face of the fiber probe tip. As any residue accumulation on this particular location can cause a significant degradation in the quality of the Raman scattering signal. One possible solution is to fit a small tube or jet aimed at the face of the fibers which can direct a cleaning solution and drying purge gas such as N_2 following a predetermined time interval. Such a system can use small amounts of a highly vaporous solvent such as acetone, xylene, or methanol that would serve to clean the fiber optic faces should they become fouled over a long period of use. Very small amounts of solvent would be used, which would eventually escape by vaporous diffusion through the gas permeable cover or membrane. These small amounts would not cause any harm to the fuel or engine systems of an airplane. In addition, a small jet of dry nitrogen directed after the solvent cleaning step can further enhance the cleanliness of the fiber faces. These types of cleaning procedures can be done automatically while the plane is being serviced for other things. The calibration of this system can also be effected using the previously mentioned cleaning jet as it can be used to direct a stream of N_2, O_2, or air to the probe volume to perform a span calibration, and by using a noble gas such as Ar or He which has no Raman scattering signature, can be used as a zero calibration.

We now discuss the claim that the fiber optically coupled Raman sensor does not pose an intrinsic ignition hazard. An accepted minimum ignition energy for jet fuel vapor in air resulting from an electrical sparks is approximately 0.25 mJ in a 1 μs duration [Chang, 2004]. This is equal to about 250 W of power over a small spark kernel that is circa 1 mm in diameter or 25 kW cm^{-2}. The laser power delivered by the present technology on the other hand is only 30 mW

which is about 8000 times less power than spark. Even when we account for the small fiber diameter of 0.20 mm, the power density is only 75 W cm^{-2}, which is a factor of over 300 less than the value from the spark ignition source. Furthermore, these values are assuming that all the power from the laser is absorbed and converted to heat before it is dissipated. The 532 nm wavelength scatters very well from metal surfaces (such as aluminum fuel tanks) with very little absorption and is optically transparent to jet fuel. Thus the laser power will diverge and be harmlessly dissipated over a broad volume without any significant thermal buildup. In the case of carbon composite fuel tanks that do absorb the laser radiation, the fuel tank surface just needs to be located several cm away from the fiber optic face to prevent a concentrated light beam from impinging on the fuel tank surface. Note that this concern is really not an issue as the gas permeable cover that surrounds and captures the laser emission permits the laser to be absorbed over a broad area with a highly broad-band scattering material that does not absorb 532 nm light readily (white colored PTFE membrane such as Gore-Tex brand membrane filters). Furthermore, the metal shield and baffles surrounding the membrane can serve as a flame arrestor should an ignition source occur within the probe volume, although that is highly unlikely given the results of the above analysis.

III. Unique or Novel Features and Benefits of Innovation

A. Unique or Novel features:

This technology permits the in-situ measurement of gaseous N_2, O_2 and fuel vapor in the ullage of a fuel tank without exposing the tank to any intrinsic explosion or fire safety hazard. The measurement technique is spontaneous laser Raman scattering which enables the simultaneous measurement of multiple chemical species. The simultaneous measurement of all major gas species enables an accurate calculation of the mixing ratio for each species without the assumption of the balance (remaining unmeasured species). The Raman measurement is implemented using fiber optic coupling which is inherently safe since there are no electrical wires that would pose an electrical ignition hazard. The fiber optic coupling also enables the sensor to be remotely located away from the excitation laser and spectrograph. The system requires little electrical power (less than 50 W). The system is compact, robust, and can be made flight hardened as the laser source is solid state. Because the laser and spectrograph/detectors are remotely located (can be in a conveniently accessible place), makes them easy to service or replace in the field. The use of the 532 nm (green) laser wavelength permits the vibrational Raman scattering signals to be measured using low-cost highly efficient visible optics such as silica fibers, highly aberration corrected anti-reflection (AR) coated camera lenses, and Si-based detectors (CCD's and APD's) that are most sensitive to red wavelengths. By using the green 532 nm wavelength, the Raman scattering efficiency is also better than by using red wavelength lasers as the Raman scattering efficiency is inversely proportional to the wavelength to the third power. Using red wavelength lasers also require the detector to be sensitive to near infrared and infrared wavelengths as the vibrational Raman shift for scattering from a 780 nm excitation laser is near 1000 nm. At these wavelengths, the sensitivity of Si-based detectors is reduced and thermal noise counts are more problematic.

B. The advantages:

There are no inherent electrical discharge ignition sources since system is fiber optically coupled. Raman scattering provides simultaneous multi-species measurement. Fiber coupling permits

remote mounting of sensor and convenient mounting of laser and spectrograph. System is compact, rugged and solid state. No consumables to wear out (as compared to electrochemical O_2 sensors). System uses little electrical power. The ability to measure N_2 concentration in addition to O_2 provides an extra measure of reliability since a true O_2/N_2 mixing ratio can be made without any assumptions of the balance gas. The mixing ratio can also be used to infer the O_2 concentration based on N_2 concentration when the O_2 density is low (such as when the pressure is low due to altitude). Multiple lasers can be used with multiple excitation fibers for in-flight redundancy. Fiber sensors can be multiplexed so that multiple sensor probes can be monitored using one laser and spectrograph. If an imaging spectrograph and CCD array detector is used, multiple sensor probes can be monitored simultaneously with only one spectrograph/detector (but multiple lasers will still be needed). Thus it is possible to monitor all three or more fuel tanks in an airplane with one spectrograph/CCD array and multiple lasers. This can save system complexity and reduce costs.

C. Development of new conceptual problems:

A major conceptual problem is optimizing the efficiency of the system so that the very weak Raman effect can be detected in a reasonable amount of time using a low amount of laser power. Typically, low power fiber optic Raman scattering systems are not used for gas-phase analysis but are used for the analysis of solids and liquids which have densities of 1000 X that of the gas phase molecules. One method that was used to enhance the efficiency was to maximize the collection volume by use of a bundle of proximity focused collection fibers surrounding a central excitation fiber. The efficiency of the sensor system was enhanced by use of a high optical throughput Raman spectrograph/polychromator as shown in Figs. 1, 6, 7, and 8 with high quantum efficiency opto-electronic detectors such as back-illuminated CCD's, PMT's, or APD's.

The conceptual problem of how to detect O_2 at cold temperatures (-1 C) and very low densities corresponding to the high altitude low pressure (0.2 atm) conditions within a reasonable time frame (1 minute) was solved by using the simultaneous Raman scattering signal from the N_2 inerting gas which has a much higher density. With the assumption that at cold temperatures the mixture of gases is predominantly O_2 and N_2, the O_2 concentration can be inferred from the much more precise measurement of N_2.

Another conceptual problem was how to build the fiber sensor probe head so that it would be robust enough to provide a durable hermetic seal between the fuel tank and the outside of the fuel tank over the wide temperature and pressure ranges of an airplane. Conventional epoxy adhesive type construction techniques would not be durable enough to withstand the effects of constant exposure to jet fuel vapor and or liquid. This problem was overcome by using Cu-clad silica fibers which enabled them to be located very close together (as there is no plastic buffer) and so that they can be hermetically sealed by soldering or brazing techniques. Note that Au-clad optical fibers are also available for the same purpose. The metal-clad fibers also have another advantage in that they do not suffer from fiber-fiber optical cross-talk.

Another conceptual problem was how to keep liquid droplets away from the fiber face located on the tip of the probe end. This problem was solved by placing a gas permeable membrane and baffles or similar structures over the tip to prevent liquid entry. This can be accomplished using various methods, with the embodiment shown in Fig. 9 being representative of the baffle-labyrinth-membrane type. Related to this is the problem of how to ensure that the fiber optic face of the sensor probe tip is kept clean from fuel residue buildup. This was solved by placing a small jet directed at fiber faces (see Fig. 9) which could inject a solvent cleaning

solution during a maintenance routine. A small vent tube connected to the probe volume chamber would then be opened to allow the exit of the contaminated cleaning solution and the subsequent dry gas cleaning purge.

Finally, the conceptual problem of how to perform a periodic in-situ calibration of the sensor was solved by using the cleaning and vents lines. These lines could be switched using electronically actuated solenoid valves to admit the calibration gases such as an inert noble gas such as argon which provides a zero gas since noble gases have no Raman scattering cross-section. Dry ambient air (passed through a desiccant pack) could be used as a convenient source of span gas as it contains 21% O_2 and 79% N_2.

D. Test data and source of error:

The fiber optic Raman sensor system was initially tested using ambient air (26 C) as the scattering medium. Figure 9 shows the Raman spectrum obtained from the present invention using 20 mW of laser power over a 90 second integration time. The data shown in Fig. 10 was acquired using the 7 fiber probe with a centrally located excitation fiber. The spectrally integrated signal for O_2 was 12,636 photon-counts (0.9% rms). The 0.9% rms represents the precision of the measurement based on Poisson statistics. If a 30 mW laser was used, similar signals can be obtained over only 60 seconds. For N_2, the spectrally integrated signal was 29,342 photon-counts (0.6% rms). The Raman scattering was actually sensitive enough to pick up the small amount of ambient water vapor 1,742 photon-counts (2.4% rms). Figure 10 clearly demonstrates the power of the fiber optically coupled Raman scattering technique to measure gas concentrations while allowing the ability to distinguish one gas species from another. In order examine the effect of jet fuel vapor on the Raman scattering signal to make sure that it does not pose any spectroscopic interferences to N_2 and O_2 bands, we insert the fiber optic probe into a cylindrical accumulator vessel that contains jet-A fuel residue (26 C) in air. Figure 11 shows the Raman data with the jet fuel vapor (solid line) collected for only a 60 second integration time. Here, we can clearly see that the jet fuel vapor has a strong Raman feature at 630 nm, there are no interferences with either N_2 or O_2. On the same plot is superimposed the data from a 10 second integration without jet fuel vapor to highlight the difference in the signal spectral shapes. The data presented in Figs. 9 and 10 show that fiber optic Raman scattering is an effective technique for measuring N_2, O_2 and jet fuel vapor in the gas phase using relatively low laser powers (20 mW).

E. Analysis of capabilities:

Using the results of Fig. 10, we calculate the system efficiency for measuring O_2 molecules as about 7 photon-counts mW^{-1} s^{-1} for about 21% O_2 by volume in air at 1 atm pressure and 26 C. This means that to get 10,000 photon-counts (1% rms) will require about 71 seconds at 20 mW. With a 30 mW laser only about 47 seconds is required. Performing the same analysis for N_2, we can see from Fig. 10 that we get 16.3 photon-counts mW^{-1} s^{-1} for about 79% N_2 by volume. This means that about 31 seconds of integration time is required to a measurement of N_2 with a precision of 1% (rms). Note that as the O_2 concentration goes down, the N_2 concentration will increase resulting in a tradeoff in the precision between the O_2 and N_2 measurements due to the N_2 enrichment. The ability to capture both O_2 and N_2 data simultaneously is a great advantage to allowing a higher level of certainty in the overall mixing ratio of O_2/N_2.

We now examine the performance of the sensor system at a challenging condition representing perhaps the lowest O_2 number density that will be encountered by the system in a

typical flight envelope: 5% O_2 by volume with balance N_2 and negligible fuel vapor, -1 C temperature, and 0.2 atm pressure [Chang, 2004]. At this condition, scaling the 7 photon-counts mW^{-1} s^{-1} for a 30 mW laser indicates that about 15.2 minutes of integration time will be required to achieve a 1% precision measurement of O_2. Clearly this is too long of a time interval for a 1% precision measurement of O_2 concentration. The advantage of the Raman scattering technique is that we simultaneously have a measurement of the inerting gas (N_2) which is at much higher concentrations. If we scale the 16.3 photon-counts mW^{-1} s^{-1} for N_2 by the 95% concentration of N_2 at this condition (by volume) and -1 C and 0.2 atm, we see that it takes only 1.28 minutes for a measurement with 1% precision. With the highly valid assumption that the fuel vapor pressure at -1 C is negligible, thus the balance of the gases simply consists of only N_2, we can infer the O_2 concentration from the following partial pressure relation: $[O_2] = 1 - [N_2]$ where the brackets indicate mole fraction. So we see that the system is capable of 1% precision measurements of O_2 concentration at low pressures within an approximately 1 minute time frame.

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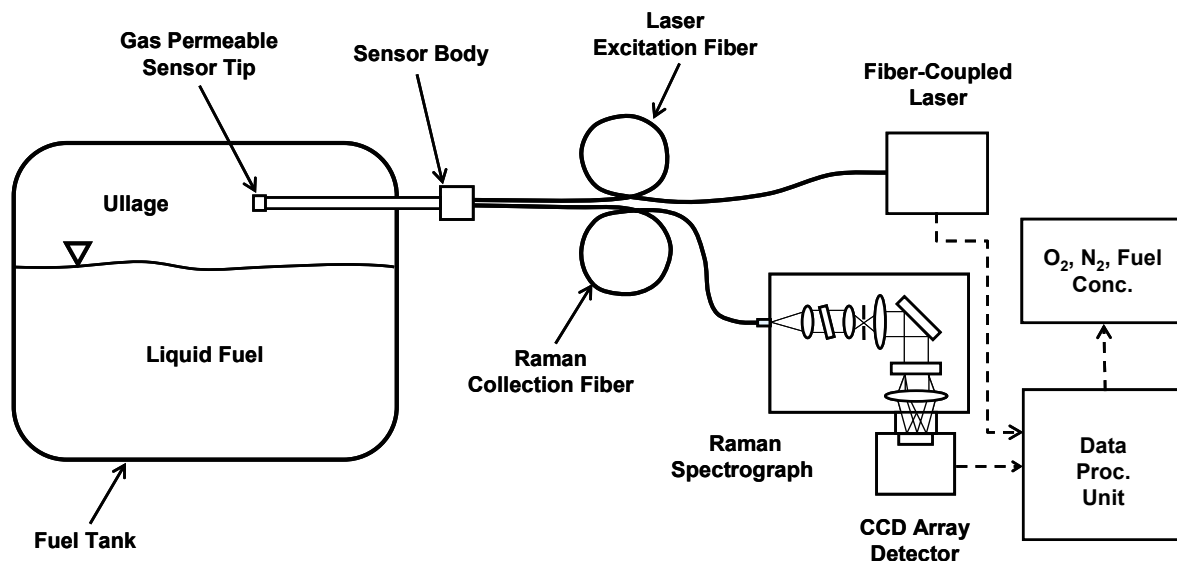
Figure 1: Schematic of fiber optic ullage oxygen/nitrogen sensor system. Fiber coupled laser is a 20 mW 532 nm diode-pumped solid state (DPSS) frequency doubled Nd:YVO$_4$. Note that other types of lasers such as Nd:YAG can also be used. The Raman spectrograph is a fast (f/1.8) axially transmissive type with holographic notch filter and holographic volume phase grating. Conventional Czerny-Turner designs can be used but have lower optical throughput. Detector is high-sensitivity thermo-electrically-cooled backside-illuminated CCD array, but discrete (or arrays of) PMT's or APD's can be used. Laser power measurement data (from laser) is used to normalize Raman signal. Fiber optic sensor probe is mounted in fuel tank with bulkhead feed through fitting. Note that the laser and spectrograph/detector array can be remotely mounted away from the harsh environment of the fuel tank.

**Fiber Probe
Sensor Body**

**Laser Excitation
(central fiber)**

**Raman Collection
(6 surrounding fibers)**

Figure 2: Schematic of end face of fiber optic probe tip (sensor end). Central fiber provides laser excitation for Raman scattering, surrounding fibers collect Raman scattered light from gas molecules in proxi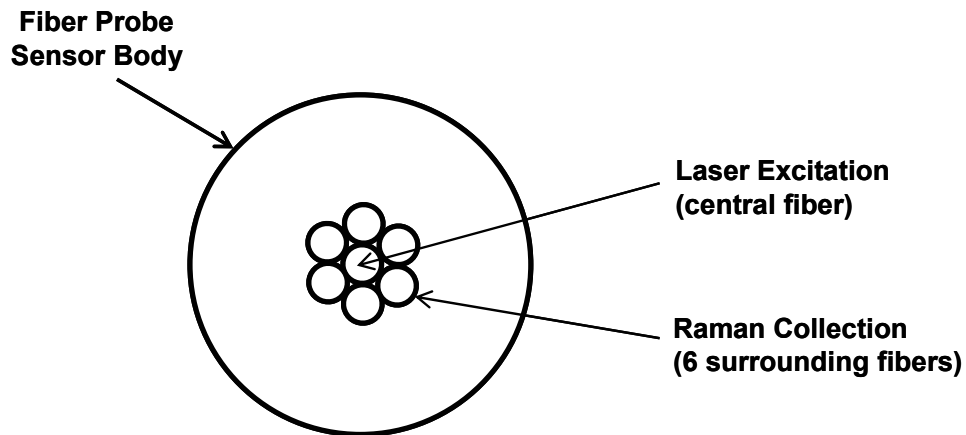mity of fiber faces. Overlap of volume between excitation fiber light cone and collection fiber cone is determined by numerical aperture (NA), diameter of fibers, and number of fibers. Although 6 collection fibers are shown, more can be used to increase collection efficiency. All fibers are multi-mode for maximum light transmission. Fibers are assembled using metal soldering or brazing techniques with special metal-clad fibers (Cu or Au). Metal clad fibers permit durable hermetic seals without fluorescence or fiber-crosstalk resulting from adhesive (epoxied) based designs. All fibers are 0.22 NA, multi-mode, Cu-clad, 200 μm dia core silica, optimized for visible transmission. Note that other fiber diameters, materials, NA, claddings can be used for the same purpose.

**Fiber Optic
Connector Tip**

**Raman Collection
Fibers
(Linear Array)**
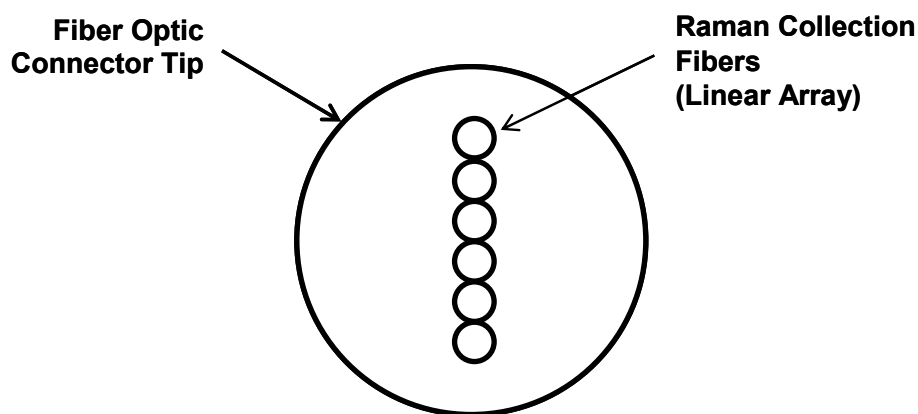
Figure 3: Schematic of fiber optic output face (Raman spectrograph end). The linear array of 6 fibers is aligned with slit axis of spectrograph to maximize Raman collection signal throughput. Physical dimension of fiber array should not exceed spectrograph slit input height, and core diameters of fibers should match the slit width of the spectrograph. In this case a slit width of 200 μm was used.

Gas Permeable Cover

Overlap Volume Between Excitation and Collection Cones

Volume between cover and sensor face does not contain liquid

Raman Collection (6 surrounding fibers)

Laser Excitation (central fiber)

End View of Sensor Tip (Gas Permeable Cover Removed)

Cross-Sectional View of Sensor Tip
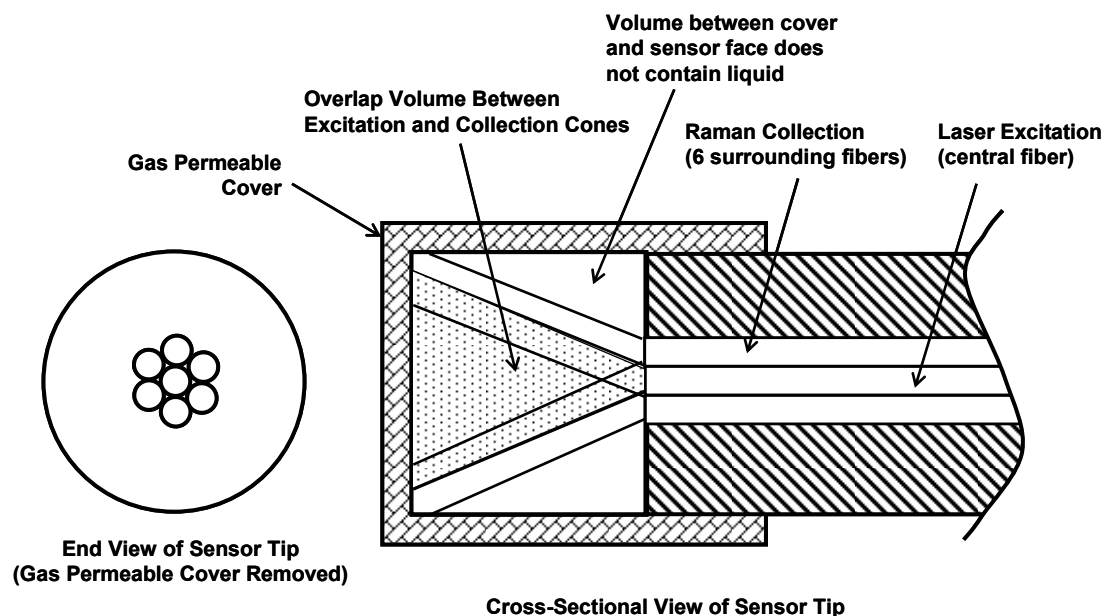
Figure 4: Schematic of end face of fiber optic probe tip (sensor end) with permeable gas cover. Cover can be a PTFE type filter membrane (e.g., Gore-Tex) or a highly porous, yet non liquid-permeable solid material with low wetability to prevent liquid fuel saturation such as a sintered polymer material. In the case of a porous membrane, the cover housing will be made of structurally rigid material to allow mounting of thin flexible membrane in correct position above the sensor face. The purpose of the gas permeable cover is to prevent liquid fuel from contacting the fiber optic face.

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│ Spectral         │     │   Acquire Raman       │     │ Current temperature, │
│ integration      │     │   spectrum over       │     │ pressure data        │
│ area definitions │     │   time t_int (60 to   │     │ for Fuel tank, and   │
│ for superpixels  │     │   90 sec)             │     │ laser power          │
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                         │ Calculate values for   │               │
                         │ each superpixel        │               │
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│ 6                │                 ▼                           │
│ Calibration data │     ┌───────────────────────┐               │
│ for each species │     │ 3  Calculate          │               │
│ (span and zero)  │────▶│    quantitative number│               │
└──────────────────┘     │    density using      │               │
                         │    calibration data   │               │
                         └───────────┬───────────┘               │
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                         ┌───────────────────────┐               │
                         │ 4    Correct for      │◀──────────────┘
                         │ temperature, pressure,│
                         │ and laser power       │
                         │ effects               │
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                         │ 5  Output N₂, O₂, Fuel│
                         │    Concentration      │
                         └───────────────────────┘
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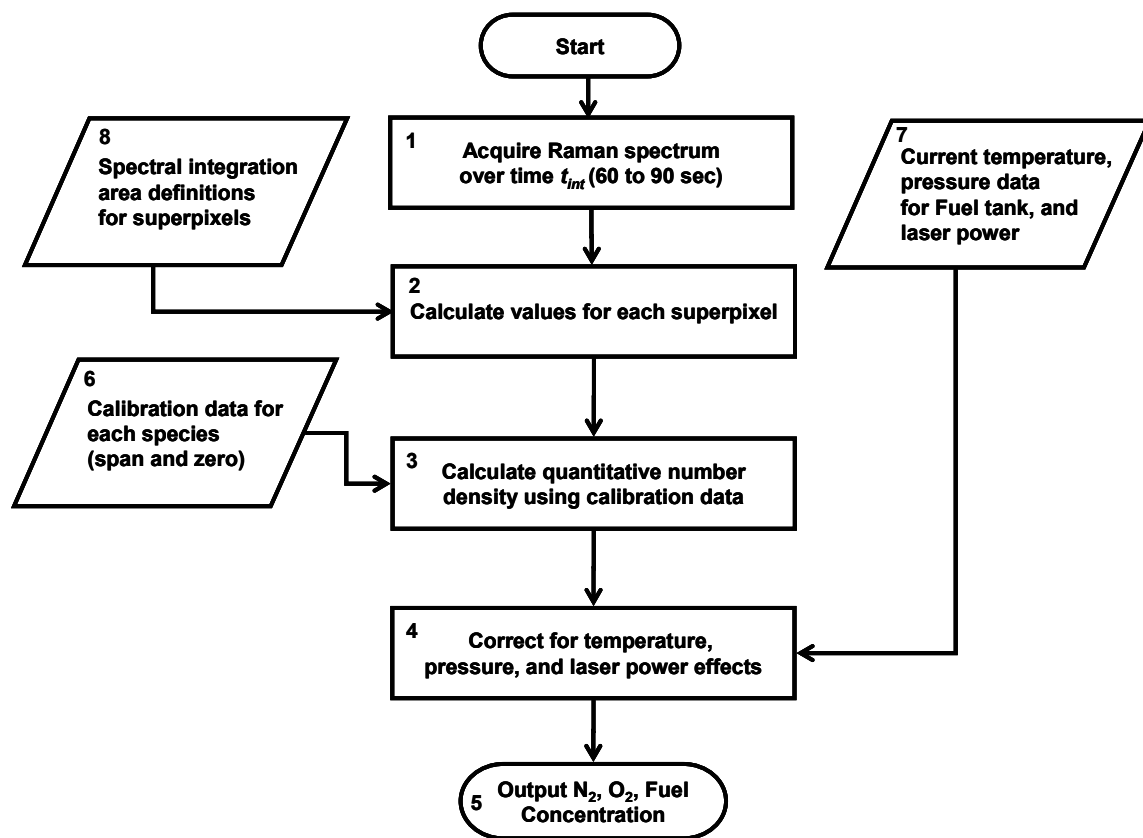
Figure 5: Block diagram of algorithm used for determination of N_2, O_2, and fuel vapor in Raman scattering ullage sensor system.
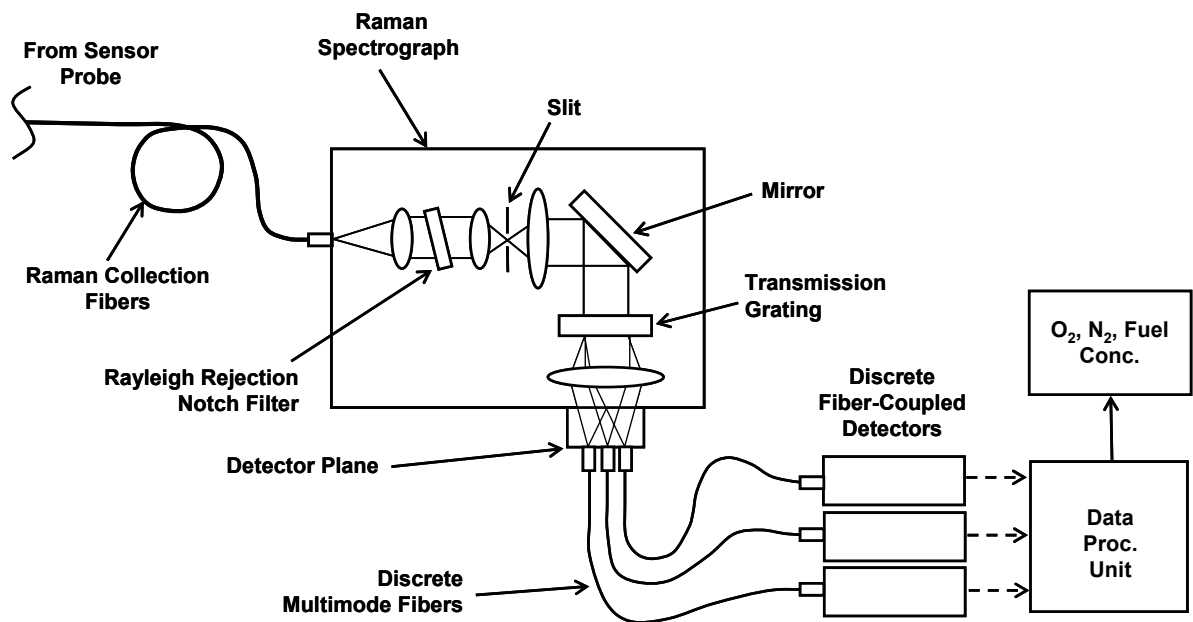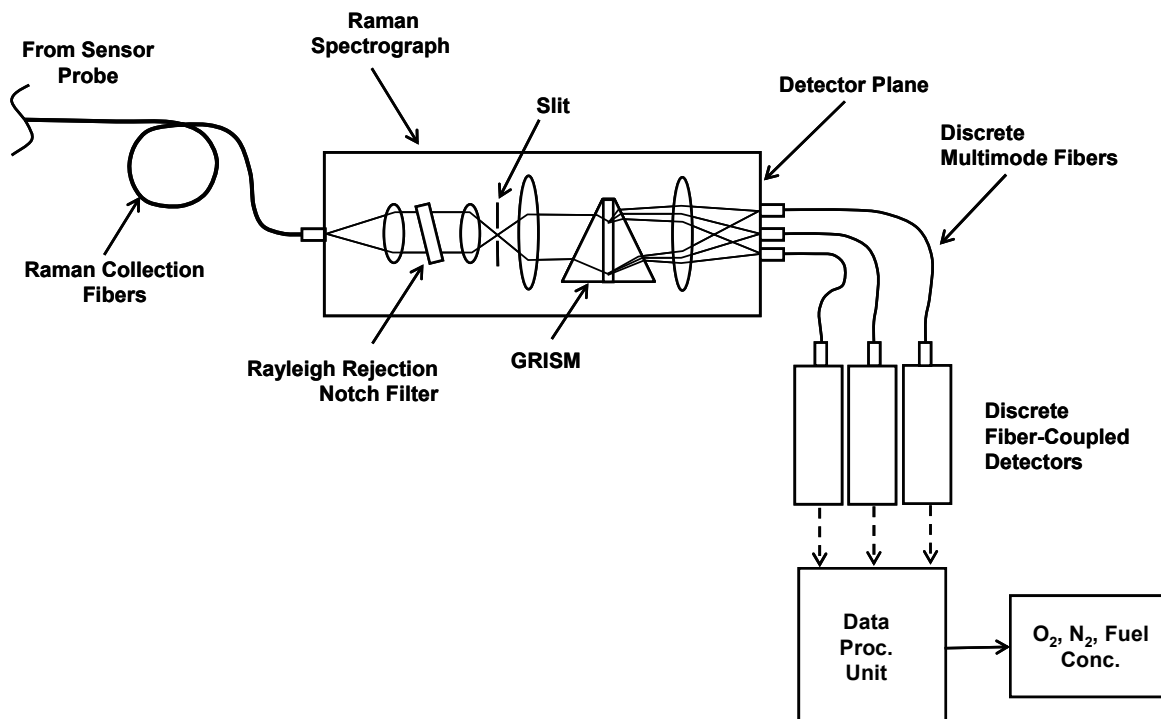
Figure 6: Schematic of alternate embodiment of system using discrete fiber optically coupled detectors (PMT, APD, etc.) mounted on the exit plane of axially transmissive holographic Raman spectrograph. Spectrograph utilizes a pre-filter section to reject elastically scattered light (Rayleigh scattering) by use of a spectral notch filter centered at laser wavelength. Such filters can be holographic volume phase filters or thin film type filters (rugate) or absorbing colored glass or molecular filters (iodine vapor, etc.). Detectors can be thermo-electrically cooled to reduce dark counts. Data processing unit still needs laser power measurement to normalize Raman signals.

Figure 7: Schematic of alternate embodiment of system using discrete fiber optically coupled detectors (PMT, APD, etc.) mounted on the exit plane of axially transmissive holographic Raman spectrograph using grating-prism (GRISM) element to provide dispersion and an undeviated path central wavelength for a compact, high optical throughput spectrograph. Note that a CCD array such as depicted in Fig. 1 can be used instead of discrete fiber optic lines at the detector plane.
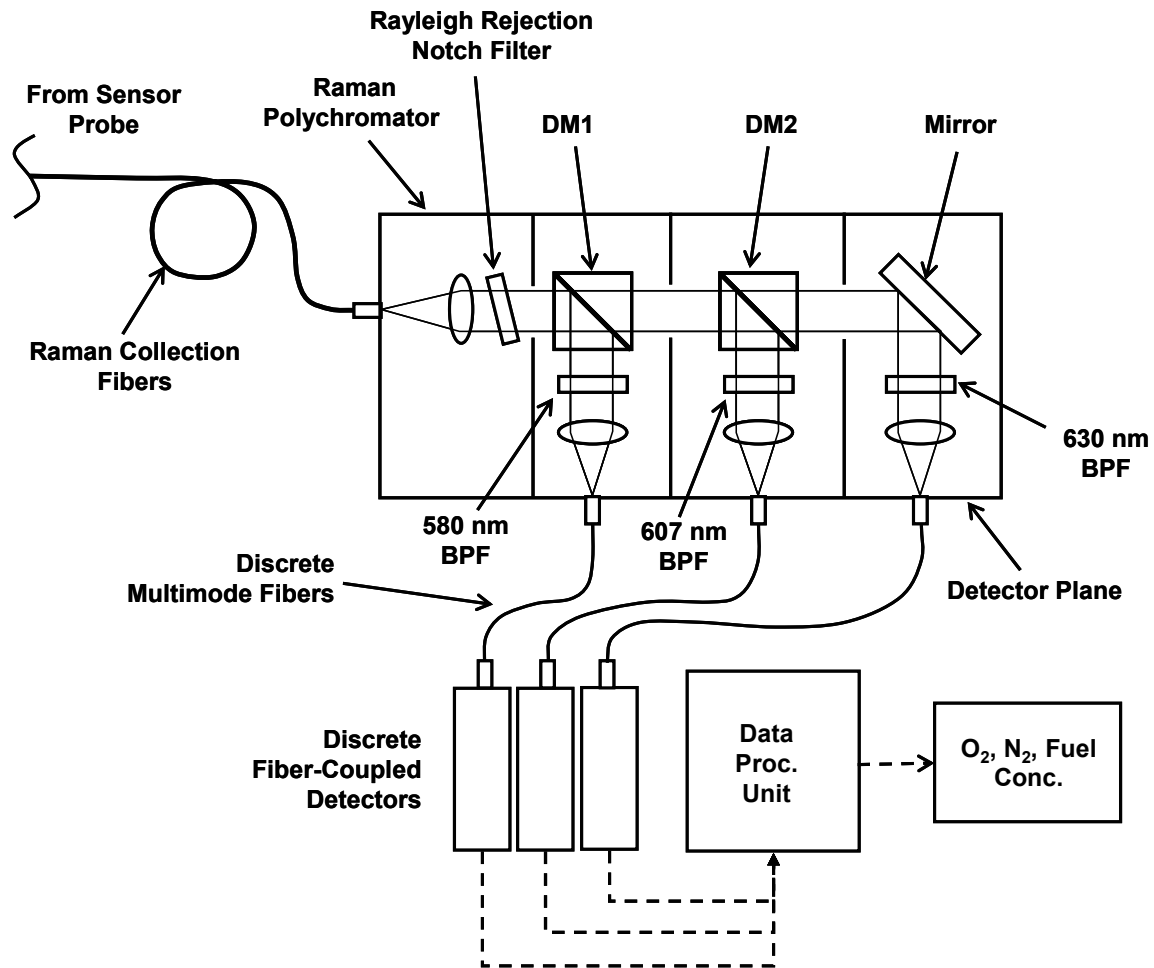
Figure 8: Schematic of alternate embodiment of system that uses dichroic beam splitters in conjunction with band pass filters to separate the Raman signal into discrete vibrational bands for detection using discrete detectors that are direct coupled or fiber optically coupled (shown). Dichroic beam splitters or mirrors transmit longer wavelengths while reflecting shorter wavelengths. Here, DM1 transmits all wavelengths > 590 nm, DM2 transmits all wavelengths > 615 nm. Band pass filters (BPF) then provide an approximate 13 nm wide bandwidth centered at 580 nm, 607 nm, and 630 nm, to transmit the Raman signal for O_2, N_2, and fuel vapor, respectively.
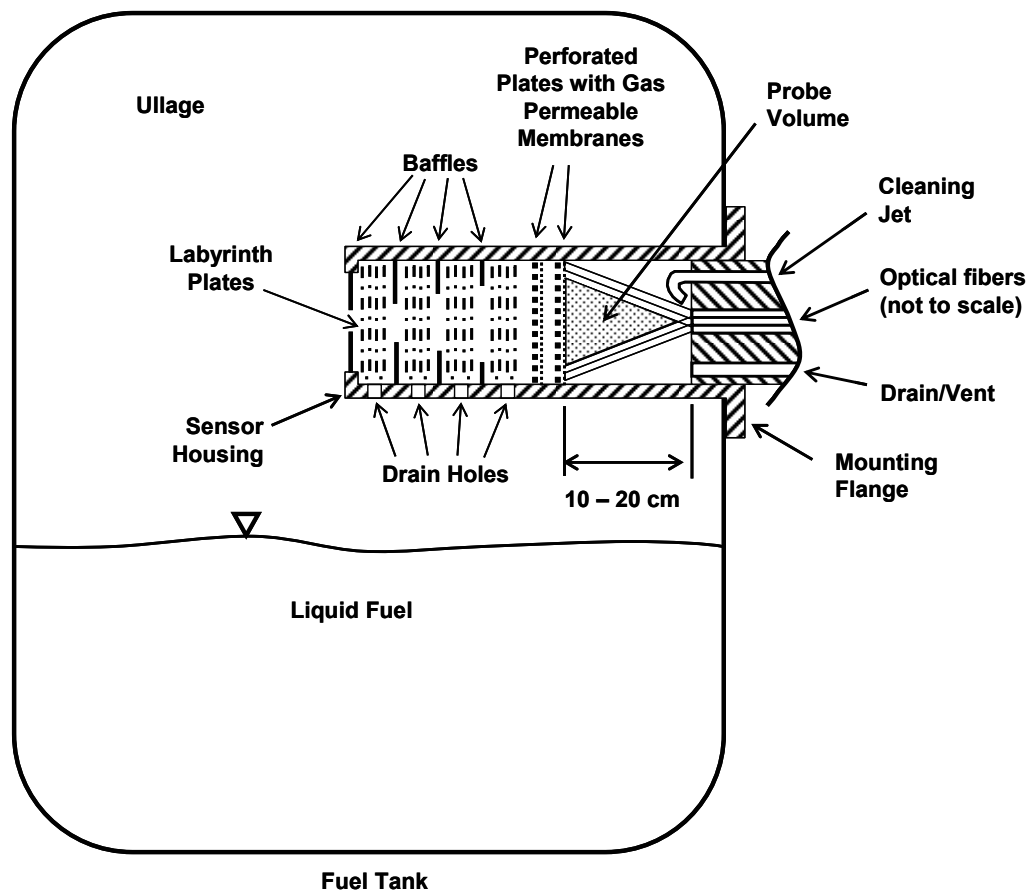
Figure 9: Schematic of alternate (and probably the preferred) embodiment of probe sensor head using a cylindrical enclosure that houses a combination of planar baffle plates with drain holes and labyrinth plates in combination with perforated metal plates that are bonded with gas permeable membranes to prevent liquid entry onto the probe volume. This sensor cover housing has a large internal volume that reduces the back scattered Raman signal contribution from the wall material itself which could be a spectral interference. The housing can be mounted to a fuel tank with a flange type seal. Additionally, a small jet aimed at the fiber faces can be used for the periodic cleaning of the fiber faces with a combination of liquid solvents and clean dry gas flows. A drain/vent tube (only open when the cleaning jet is used) permits the contaminated cleaning solvent to be removed.
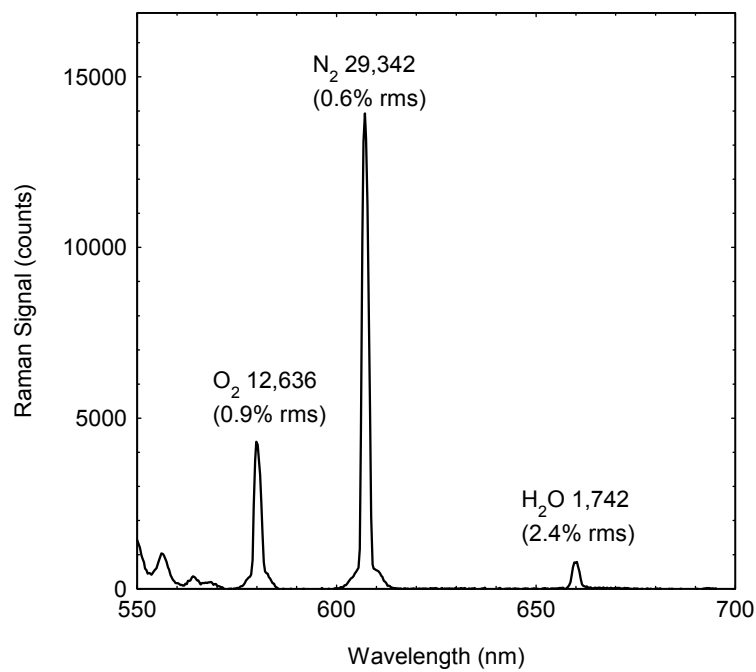
Figure 10: Data showing signals from ambient air (26 C) acquired using fiber optic Raman sensor probe. Spectrum was acquired in 90 seconds using 20 mW of 532 nm laser excitation from a DPSS Nd:YVO$_4$ laser. The CCD detector was cooled to -115 C to minimize dark counts. Vibrational band integrated signal values are shown above for each species; signal root-mean-square (rms) values represent one standard deviation (precision) of integrated values assuming Poisson statistics. Note that even ambient water vapor was detected. Data was obtained without gas permeable sensor cover.
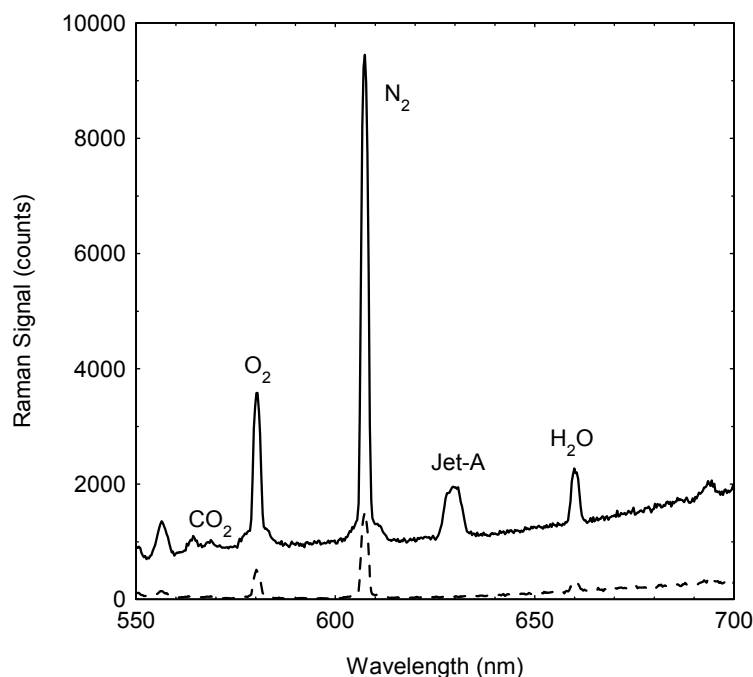
Figure 11: Data showing signals from jet-A fuel vapor mixed with ambient air (26 C) acquired using fiber optic Raman sensor probe (solid curve) over a 60 second exposure; the dashed curve shows the spectrum for air only with only a 10 second exposure. Spectrum was acquired using 20 mW of 532 nm laser excitation with the CCD detector cooled to -115 C. The vibrational bands for each species are centered at the following wavelengths: 580 nm, 607 nm, and 630 nm, for O_2, N_2, and jet-A, respectively. By using a 13 nm wide spectral window for each vibrational band, the entire O-Q-S bands can be collected to maximize the signal while minimizing the background noise. The sensitivity of the system enables even ambient water vapor and carbon dioxide to be detected. The data with the jet-A fuel vapor was obtained by placing the probe inside a small cylindrical accumulator vessel to simulate a fuel tank; the fuel tank walls caused some fluorescence background visible as the upward slope. However, this can easily be subtracted during the data processing as it is a constant. Data shown was obtained without a gas permeable sensor cover.